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13. ABSTRACT (Maximum 200 words)  New azulene-containing chromophores were synthesized and their nonlinear optical and excited state properties determined in collaboration with Natick ARO and academic researchers. DFWM and two-dimensional Z-scan measurements revealed that an azulenic polymethine dye, a new class of NLO chromophore, was an effective optical power limiter. A series of azulenic polymethine dyes were prepared and their third-order NLO activity and optical power limiting thresholds determined. Third-order susceptibilities were enhanced by increasing conjugation length and side-chain alkylation. First hyperpolarizabilities were determined by the Hyper-Raleigh Scattering method at 1064 and 1907 nm for several new azulenic chromophores. New polymers containing azulenic NLO chromophores were prepared for the first time. Dramatic enhancement of azulene fluorescence was realized by manipulation of excited state energy gaps by molecular engineering. Theoretical calculations provided structural guidelines for the preparation of new azulenic NLO chromophores.			
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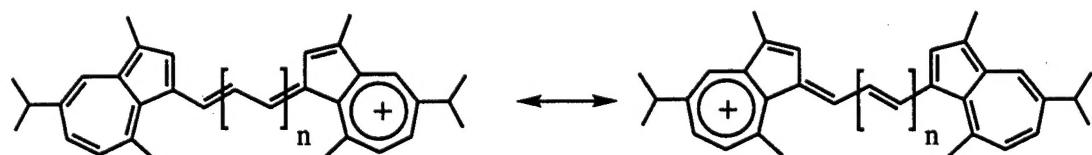
## 1. Introduction and Background

Organic materials are in great demand for optoelectronic applications because of their useful nonlinear optical properties and the ease with which these properties can be manipulated by judicious molecular engineering. Our studies have focused on the preparation of highly polarizable, conjugated NLO compounds containing the versatile  $\pi$ -electron donor, azulene. These novel second- and third-order NLO compounds are primarily intended for optical power limiting applications such as optical sensor and eye protection. We earlier established that azulenic donor-acceptor chromophores had large second-order optical nonlinearities and excellent thermal stabilities. As the  $\pi$ -electron in NLO chromophores of the same conjugation length and with the same acceptor groups, azulene was entirely equivalent to (or better than with respect to thermal stabilities) the commonly used aromatic amine donor, *para*-N, N-diethylaniline.<sup>1</sup>

## 2. Summary of Scientific Progress and Accomplishments

### a. Azulene-containing polymethine dyes have large third-order susceptibilities and are optical power limiters.

In a collaborative structure-NLO activity relationship study with Dr. Masato Nakashima and co-workers at Natick ARO and Professor D. V. Rao and co-workers at U. Mass-Boston, azulenic polymethine cationic dyes were identified as a new class of third-order NLO chromophore.<sup>2,3</sup> The new compounds are thermally stable and absorb strongly in the near-infrared region with very little light absorption in the visible region. Except for the shortest member of this series ( $n = 0$ ), these dyes are all reverse saturable absorbers and display optical power limiting.



$n = 0-4$

The gain (or loss) of aromaticity in NLO molecules strongly affects charge separation and molecular hyperpolarizabilities.<sup>4</sup> Delocalization of  $\pi$ -electrons in the new azulenic NLO dyes is very efficient because, upon charge separation, a new resonance stabilized Hückel 6  $\pi$ -electron aromatic azulenylium (tropylium) carbocation is formed. In other words, disruption of conjugation is not a problem in azulenic cationic dyes since neutral azulene and azulenylium carbocation are both stabilized by aromaticity. This special stabilization is absent in conventional donors (*para*-N,N-disubstituted anilines or sulfur heterocycles) which lose aromatic stabilization upon charge separation.

The compounds were studied in solution using degenerate four wave mixing (DFWM) and the z-scan technique at 532 nm with 30 ps pulses. Extrapolated values for the third-order nonlinear optical susceptibility  $\chi^{(3)}$  of the compounds were in the range  $10^{-9}$  to  $10^{-8}$  esu. Z-scan results indicated reverse saturable absorption. Optical power limiting with a f/5 system was demonstrated for all of the compounds studied.

Professor Peter Rentzepis of U. C. Irvine has also collaborated with Natick ARO and our group to determine nonlinear optical and excited state properties of several of our novel azulene-type donor-acceptor compounds by his very useful two-dimensional Z-scan technique.<sup>5,6</sup> These compounds exhibit considerable nonlinear refraction and one shows strong nonlinear saturated absorption at 527 nm. The transient spectra and kinetics, after excitation of the charge-transfer absorption band, have been studied by means of a picosecond transient absorption spectroscopy. Absorbance changes as small as  $\Delta A = 0.005$  and time resolution of 1.5 ps were routinely measured. Several compounds exhibited quite strong reversed saturable absorption in a wide region of the visible spectrum. The reversed saturable absorption induced an increase in the effective absorption of the material at high power, which suggests that, it may be useful as an optical limiting medium.

In collaboration with Professor C. H. Wang of U. Nebraska-Lincoln, Hyper-Rayleigh scattering (HRS) measurements were carried out for new azulenic donor-acceptor chromophores using near infrared laser excitation at wavelengths of 1064 nm and 1907 nm.<sup>7</sup> First molecular hyperpolarizabilities obtained with the 1064 nm incident excitation are large compared with those obtained using the 1907 nm excitation, due to the one and two photon resonance enhancements in the former case. The HRS experiment using the 1907 nm excitation, while challenging to carry it out, gives the hyperpolarizability value closer to the intrinsic molecular hyperpolarizability. The

popular two-level model that is used to predict the first hyperpolarizability of donor-acceptor charge transfer chromophores is employed to compare the measurements made on the same chromophores with 1064 and 1907 nm excitations. The model is found not to be able to correlate the results obtained at the two wavelengths.

**b. The excited state properties of azulene and azulenic NLO chromophores can be regulated by molecular engineering.**

We made significant progress in understanding the effects of various structure modifications on excited state properties (fluorescence) of azulene and its derivatives including donor-acceptor chromophores.<sup>8,9</sup> The energy difference between the very low-lying first excited state  $S_1$  and the second excited state  $S_2$  can be manipulated by appropriate substitution at the 1- and 3-positions--a simultaneous control of the excited state lifetime. Electronegative fluorine substituents cause an increase of the gap while electron-withdrawing conjugated appendants close the gap. The effectiveness of the azulene as a donor in a donor-acceptor chromophore can be further enhanced by strategic placement of other substituents on the  $\pi$ -system (e.g., alkyl groups on the ring). The dipolar characteristic of the chromophore has been incorporated into the design of new Near-IR absorbing chromophores. The half-linewidth of the absorption band can be regulated by the proper choice of solvent or judicious structural modification

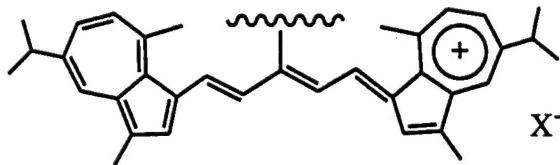
**c. Oxidation-reduction potentials were determined for azulenic NLO chromophores.**

Electrochemical properties of our azulenic compounds were measured by cyclic voltammetry. Oxidation and reduction potentials correlate with HOMO and LUMO energies, respectively. A linear relationship between redox potentials and Hammett constants was also revealed for a large series of azulenic azobenzenes substituted with fluorine and other electron-withdrawing substituents. Since the Hammett free energy relationship provides a measure of the  $\pi$ -electron acentricity in donor-acceptor molecules, it follows that redox potentials are also a measure of electron asymmetry, and correspondingly, first hyperpolarizabilities, in our compounds. Solvatochromism, another important property associated with  $\pi$ -electron mobility

and enhanced hyperpolarizability, was also observed for several second-order chromophores with strong acceptor groups.

**d. Azulenic NLO chromophores can be incorporated into polymers.**

We also incorporated several azulenic NLO into polymers both by doping and covalent attachment of the chromophore to the polymer chain. In one case we converted the pyridine pendant group of a copolymer, poly(styrene-*co*-4-vinylpyridine), to a cyanine dye and, thereafter, to a guaiazulenic pentamethine dye with  $\lambda_{\text{max}} = 901$  nm.



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The guaiazulenic pentamethine monomer was previously shown by the Natick ARO group to be an optical power limiter. Although further work on the copolymer stoichiometry is necessary to improve solubilities and other properties, this is the first example of an optical power limiting material with an azulenic dye covalently attached to a polymer host. We have also explored the preparation of polystyrene and PMMA films doped with azulenic NLO chromophores to assess light and air stability, and qualitatively measure linear electronic absorption properties. Further work in this area is in progress.

**e. Theoretical calculations of electronic and nonlinear optical properties of azulene-containing NLO chromophores point to useful structural modifications to improve optical nonlinearities and other properties.**

An understanding of the electronic properties of our azulenic NLO chromophores is clearly useful for the rational design of new molecules with enhanced optical limiting and other NLO properties. Quantum mechanical calculations of molecular hyperpolarizabilities and electronic

properties of some azulene-containing chromophores were carried out using the AM1/FF and ZINDO/S-CI approach.<sup>9,10</sup> The calculated results were in good agreement with experimental values. With donor groups on the seven-membered ring of azulene it becomes a more efficient conjugation bridge compared to either benzene or thiophene. We ascribe this to the lower delocalization energy of the nonalternant aromatic hydrocarbon. Enhanced first hyperpolarizabilities can be obtained by extending conjugation length, altering substituent positions or choosing appropriate substituents. Rather unexpectedly, azulene with a donor group on the 1-position of the five-membered ring and an acceptor on the 5-position of the seven-membered ring was found to have a large  $\beta$ -values and small dipole moment. These properties will be helpful in reducing chromophore-chromophore electrostatic interactions and in optimizing the chromophore loading level and the order parameter when incorporated into a polymer matrix.

### 3. Summary

In collaboration with Army scientists at Natick ARO and several academic researchers we demonstrated the utility of our azulene-containing compounds for NLO applications. A new class of NLO chromophore, the azulenic polymethine dyes, were shown to be effective optical power limiters. First molecular hyperpolarizabilities for several new azulenic donor-acceptor compounds were determined by Hyper-Raleigh Scattering technique. Oxidation-reduction potentials were also measured by cyclic voltammetry for the new chromophores. Excited state properties (fluorescence) were greatly enhanced by appropriate molecular engineering of azulene. Finally, we identified key structural features that control NLO properties and verified theoretically by quantum chemical calculations various ground and excited state electronic properties.

#### 4. References

1. Asato, A. E.; Liu, R. S. H.; Rao, V. P.; Cai, Y. M. "Azulene-Containing Donor-Acceptor Compounds as Second-Order Nonlinear Chromophores," *Tetrahedron Lett.* **1996**, *37*, 419-422.
2. Kimball, B. R.; Nakashima, M.; Cristofano, B. S.; Aranda, F. J.; Rao, D. V. G. L. N.; Asato, A. E.; Liu, R. S. H. "Third-Order Nonlinear Optics of Some Azulenic Donor-Acceptor Compounds," *SPIE Proceedings* **3473** **1998**, 101-111.
3. Kimball, B. R.; Nakashima, M.; Decristofano, B. S.; Panchangam, A.; Bhadra, S. K.; Rao, D. V.; Aranda, F. J.; Asato, A. E.; Liu, R. S. H. "Optical Power Limiting in Some Azulenic Compounds," *SPIE Proceedings* **3798** **1999**, 32-37.
4. G. Bourhill, L.-T. Cheng, C. B. Gorman, G. Lee, S. R. Marder, J. W. Perry, M. J. Perry, and B. G. Tiemann, "Experimental demonstration of the relationship between second- and third-order polarizabilities of conjugated donor-acceptor molecules," *SPIE Proceedings* **2143** **1994**, 153-163.
5. Oulianov, D. A.; Chen, P.; Tomov, I. V.; Rentzepis, P. M. "Investigation of Benzoporphyrin and Azulenic Compounds by Two-Dimensional Z-Scan Technique," *SPIE Proceedings* **3472**, **1998**, 98-105.
6. Oulianov, D. A.; Tomov, I. V.; Dvornikov, A. S.; Rentzepis, P. M. "Nonlinear Properties and Kinetics of Some Donor-Acceptor Optical-Limiting Molecules," *SPIE Proceedings* **3798**, **1999**, 101-106.
7. Woodford, J. N.; Wang, C. H.; Asato, A. E.; Liu, R. S. H. "Hyper-Raleigh Scattering of Azulenic Donor-Acceptor Molecules at 1064 and 1907 nm," *J. Phys. Chem.*, in press.
8. Wang, P.; Zhu, P.; Ye, C.; Asato, A. E.; Liu, R. S. H. "Theoretical Investigation and Molecular Design of Some Azulene Derivatives with Large Hyperpolarizabilities," *J. Phys. Chem.* **1999**, *103*, 7076-7082.
9. Liu, R. S. H.; Muthyalu, R. S.; Wang, X.-S.; Asato, A. E.; Wang, P.; Ye, C. "Correlation of Substituent Effects and Energy Levels of the Two Lowest Excited States of the Azulene Chromophore," submitted to *Org. Letters*.
10. Tetreault, N.; Muthyalu, R. S.; Liu, R. S. H.; Steer, R. P. "Control of the Photophysical Properties of Polyatomic Molecules by Substitution and Solvation: The Second Excited Singlet State of Azulene," *J. Phys. Chem.* **1999**, *103*, 2524-2531.

## 5. List of Publications for Performance Period

1. Liu, J.; Liu, R. S. H.; Simmons, C. J. "Synthesis and Properties of Arylspiralene. A Cisoid Z, Z-1,4-Diphenyl-1,3-butadiene," *Tetrahedron Lett.*, **1997**, *38*, 3999-4002.
2. Bell, J. R.; Muthyala, R. S.; Larsen, R. W.; Alam, M.; Liu, R. S. H. "Photoactivities of the Red-Shifted Azulenic Bacteriorhodopsin Analogues," *J. Phys. Chem.* **1998**, *102*, 5481-5483.
3. Kimball, B. R.; Nakashima, M.; Decristofano, B. S.; Aranda, F. J.; Rao, D. V. G. L. N.; Asato, A. E.; Liu, R. S. H. "Third-Order Nonlinear Optics of Some Azulenic Donor-Acceptor Compounds," *SPIE Proceedings 3473* **1998**, 101-111.
4. Oulianov, D. A.; Chen, P.; Tomov, I. V.; Rentzepis, P. M. "Investigation of Benzoporphyrin and Azulenic Compounds by Two-Dimensional Z-Scan Technique," *SPIE Proceedings 3472* **1998**, 98-105.
5. Imai, H.; Hirano, T.; Terakita, A.; Shichida, Y.; Muthyala, R. S.; Chen, R.-L.; Colmenares, L. U.; Liu, R. S. H. "Probing for the Threshold Energy for Visual Transduction. Red-shifted Visual Pigment Analogs from 3-Methoxy-3-dehydroretinal and Related Compounds," *Photochem. Photobiol.* **1999**, *70*, 111-115.
6. Wang, P.; Zhu, P.; Ye, C.; Asato, A. E.; Liu, R. S. H. "Theoretical Investigation and Molecular Design of Some Azulene Derivatives with Large Hyperpolarizabilities," *J. Phys. Chem.* **1999**, *103*, 7076-7082.
7. Tetreault, N.; Muthyala, R. S.; Liu, R. S. H.; Steer, R. P. "Control of the Photophysical Properties of Polyatomic Molecules by Substitution and Solvation: The Second Excited Singlet State of Azulene," *J. Phys. Chem.* **1999**, *103*, 2524-2531.
8. Kimball, B. R.; Nakashima, M.; Decristofano, B. S.; Panchangam, A.; Bhadra, S. K.; Rao, D. V.; Aranda, F. J.; Asato, A. E.; Liu, R. S. H. "Optical Power Limiting in Some Azulenic Compounds," *SPIE Proceedings 3798* **1999**, 32-37.
9. Oulianov, D. A.; Tomov, I. V.; Dvornikov, A. S.; Rentzepis, P. M. "Nonlinear Properties and Kinetics of Some Donor-Acceptor Optical-Limiting Molecules," *SPIE Proceedings 3798* **1999**, 101-106.
10. Woodford, J. N.; Wang, C. H.; Asato, A. E.; Liu, R. S. H. "Hyper-Raleigh Scattering of Azulenic Donor-Acceptor Molecules at 1064 and 1907 nm," *J. Phys. Chem.*, in press.
11. Liu, R. S. H.; Muthyala, R. S.; Wang, X.-S.; Asato, A. E.; Wang, P.; Ye, C. "Correlation of Substituent Effects and Energy Levels of the Two Lowest Excited States of the Azulene Chromophore, "submitted to *Org. Letters*.

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